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(54) METHOD OF PRODUCING RESIN-CONTAINING PIGMENT PREPARATIONS

- (71) We, KEMISK VAERK KOGE A/S, a Danish Company of 39, Overgaden neden Vandet, Copenhagen, Denmark, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- This invention relates to the production of a particulate organic pigment preparation which comprises particles of a resin and an organic pigment, the pigment being dispersed within the resin particles. Such preparations need to be readily dispersible and are of value for the production of paints, varnishes, printing inks, plastics and plastic-ware.
- Various ways of producing organic pigment preparations of this general type are known but the methods are often not very convenient to operate and the resulting pigment preparation often does not have as satisfactory pigmenting properties as would be desired. A particular problem is that the existing methods do not allow the production of preparations containing a large amount of pigment dispersed through the particles.
- One known method for the production of pigment-resin compositions comprises working pigment into a resin softened by heating using a powerful mechanical treatment, and thereby forming pigment chips. Another method comprises milling the pigment in the presence of water and an organic solvent that is miscible with water. If desired a small amount of a water immiscible organic solvent for the resin can be present. Such a method is described in Specification No. 768,844 from which it is apparent that a combination of water, water miscible solvent and water immiscible solvent results in the formation of a liquid phase containing all three liquids.
- According to the invention we make a particulate pigment preparation comprising particles of a resin and organic pigment dispersed within the resin particles, the pigment being present in the particles in an amount of 70% or more by weight based on the total weight of resin and pigment.
- A method according to the invention of forming particles of resin having organic pigment uniformly dispersed therein comprises mixing the resin in particulate form, organic pigment in an amount of 70% or more by weight based on the total weight of resin and pigment, water and an organic liquid, or organic liquid mixture, that is immiscible with water and is incapable of dissolving the resin but which is absorbed in the resin and thereby forms an organic solid phase comprising the resin, pigment and organic liquid or liquids and an aqueous phase that is substantially free of organic liquid, and separating the aqueous phase from the solid phase.
- By this method pigment preparations in which the particles contain 70% or more of the pigment, for example 75 to 80% or more, are obtained. Another advantage is that the mechanical treatment necessary for mixing does not have to be more than has been required in previous processes and in fact can usually be a less powerful mechanical treatment or can be conducted for a shorter time. Another advantage is that a much smaller proportion of organic liquid is needed than has been needed previously. Another advantage is that in many cases the preparation obtained on drying the solid phase is in a powdery form while in other cases it is obtained in the form of grains or lenses. These can easily be ground to powder or may be useable without grinding.
- It will be appreciated that in the method of the invention the organic liquid or liquids are immiscible with water and there is no, or insignificant, dissolution of organic liquid in

the water. In the prior method there has always been a large amount of water miscible solvent, for example acetone so that the aqueous phase is an aqueous organic solvent phase in equilibrium with a resin-containing phase which also contains water and organic solvent.

In the invention the water is present solely for the purpose of facilitating the mixing process and for ensuring that discrete particles are obtained.

The resin, pigment, water and organic liquid are usually mixed together by first mixing the pigment with water and then adding the resin and organic liquid. Suitable methods of mixing the composition involve milling processes using for instance a ball mill, a vibrator mill or an attritor or by using rapidly rotating stirrers, for instance those of Cowles, Greaves or the "Kady" mill ("Kady" being a Trade Mark) or using a colloid mill. By way of example, the method may be carried out by introducing in a ball mill suitable grinding bodies, such as spheres, and dry pigment or an aqueous pigment paste together with an amount of water sufficient to secure that an easily flowing paste is formed in the mill. The ball mill is then closed and allowed to run for a short time, say half an hour to one hour, in order to homogenize the mixture. Then an organic liquid suitable for the resin to be used is introduced and the mixture is again homogenized. After homogenization, finely pulverized resin is added and the mill is rotated for a suitable number of hours. During the milling process the pigment, the resin and the organic liquid separate from the water to form a phase varying as to its form from a crystalline powder to granules or lenticular plates freely movable in the water phase. The whole mass can be washed out from the ball mill with water, whereby after filtration a water wetted product consisting of pigment, resin and organic liquid is obtained. After evaporation of adhering water and organic liquid the pigment preparation consisting of finely dispersed pigment incapsulated in resin is obtained. The preparation thus obtained may be ground to powder if desired.

Another way of mixing involves the use of a rapidly rotating stirrer and in this an aqueous pigment paste and, when necessary, an appropriate further amount of water are placed in a vessel after which the mass is homogenized and dispersed by means of the rapidly rotating stirrer. Usually a dispersing agent suitable for the pigment in question is added, this being of a kind the dispersing effect of which can be broken at a later stage of the process. Then pulverized resin is added and stirring is continued for half an hour to one hour. If a dispersing agent has been added the effect thereof is then broken and a

suitable organic liquid is added. As a result the pigment, the resin and the organic liquid gather to form small grains and a water phase separates in which the grains are freely movable. After continuing the stirring for still another quarter of an hour to half an hour the particles of pigment-resin, the organic liquid contained therein as well as any excess of organic liquid and adhering water are removed from the filter residue by evaporation. After crushing, if necessary, the desired pigment preparation has been obtained.

By reason of the short time of treatment the production by means of rapidly rotating stirrers offers the possibility of obtaining a greater production capacity than when using a ball mill.

The choice of organic liquid or liquids is important. It is necessary that in the method the resin does not dissolve in the liquid, i.e. a solution of resin in liquid is not formed. However the liquid must be one that is capable of being absorbed by the resin. Thus it can be considered as becoming dissolved in the resin. This must of course be contrasted to the situation when the resin is dissolved in the liquid. Dissolution, or absorption, of the liquid in the resin involves the liquid being absorbed into the structure of the resin without destroying this structure. Swelling of the resin will normally accompany this absorption.

The applicability of a given liquid or liquid mixture for use with a particular resin can be ascertained by pouring an amount of the liquid or liquid mixture upon the resin while it is in particulate condition. If the liquid or mixture is suitable for use in the invention it will be absorbed by the resin to produce a product which, on rolling between the fingers, has low coherence, i.e. it substantially maintains its particulate nature, and which is generally transparent. If a surplus of the liquid is used then a two phase system will form, the liquid phase consisting of the liquid that has been added.

Although this appears a simple criterion for the selection of a suitable liquid or liquid mixture in practice the selection can be more difficult, for example when a pigment preparation is being prepared using widely different resins. It is therefore convenient to select the organic liquid or liquids according to particular physical data that are obtainable for the liquid or liquids and for the resin. Thus use is made of the known "solubility parameter value" of a possible liquid or mixture of liquids, combined with the knowledge of the "solubility parameter interval" of the resin under consideration. These terms are known terms and are discussed by, for example, H. Burrell in Official Digest 1955, 27, No. 369, page 726, P. Sorensen in Journal of Oil and Colour

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Chemists Association 1967, volume 50, No. 3, page 226 and C. M. Hansen in "The Three Dimensional Solubility Parameter" Danish Technical Press 1967. The solubility parameter value of the liquid or liquids is a numerical constant having the dimensions $\text{cal}^{1/2} \times \text{cm}^{3/2}$. The value can be calculated on the basis of the physical properties of the liquid.

Suitable organic liquid or liquid mixtures for use in the invention are those in which the solubility parameter of the liquid or mixture has a value substantially immediately above or substantially immediately below the solubility parameter interval of the resin under consideration.

The solubility parameter intervals of resins cannot be calculated because such substances are mixtures of a number of different molecular species with different molecular weight, said species being partially unknown. They must be determined experimentally with respect to each kind of solvent. For this purpose solvents are divided in the following three groups:

Group I comprising weakly hydrogen-bonded solvents such as aliphatic or aromatic hydrocarbons which may be chlorinated or nitrated,

group II comprising moderately hydrogen-bonded solvents such as ethers, esters and ketones and

group III comprising strongly hydrogen-bonded solvents such as alcohols, amines and acids.

The solubility parameter value intervals of resins are generally published by the manufacturer or can be experimentally determined. The values are usually subject to an uncertainty of 0.4 delta units.

In the case of solvents where the solubility parameter can be calculated the solubility parameter value of a mixture of two or more liquids belonging to the same group can be calculated by simple proportionating. Some examples illustrates the method.

Ethyl cellulose has with respect to solvents of group I the solubility parameter interval 8.1-11.1. The liquids petrol 100/140 and xylene have the solubility parameter values 7.6 and 8.8, respectively, which means that xylene dissolves in ethyl cellulose whereas petrol does not. From 85 g of the said petrol and 60 g xylene a mixture can, however, be produced of which the parameter value is $(85 \times 7.6 + 60 \times 8.8) : (60 + 85) = 8.1$ which mixture is suitable for use in connection with ethyl cellulose. If the liquids belong to different groups the useful ratio must be estimated.

Another example is a resin "vinylit VYHH" which, according to the information of the manufacturers, has a solubility parameter value interval of 9.3-11.1 with

respect to solvents of group I, and 7.8-13.3 with respect to solvents of group II. The group I—solvent xylene has the solubility parameter value 8.8, whereas the group II—liquid methylbutyl ketone has a value 8.4. The latter solvent dissolves vinylit VYHH whereas xylene does not. Since xylene is placed 0.5 delta units below the solubility parameter value interval of vinylit VYHH with respect to group I and since methyl-isobutyl ketone is placed .68-units above the lower limit of the interval with respect to group II it is estimated that 6 parts of xylene and 5 parts of methyl-isobutyl ketone will constitute the correct mixture. Also a mixture consisting of equal parts of the two solvents is suitable. With benzene the same result could have been obtained but the above named mixture is preferable from a practical point of view because of the low flash-point of benzene which makes the use of this hydro-carbon difficult. Even other circumstances may influence the choice of solvents. Thus in the case of pigmented varnishes it is unsatisfactory to use liquids belonging to the groups II and III which would depreciate the lacquer.

By way of example of applications of the pigment preparations produced according to the present invention may be mentioned that copolymers of vinyl chloride and vinyl acetate are suitable as binders in paints and printing inks for gravure for which reason pigment preparations containing such copolymers are suitable for colouring such paints and printing inks, considerably improved results being obtained compared to conventional grinding of the pure pigments with a solution of the binding agent. Thus the coloured coating obtained is considerably more glossy and transparent. The pigment preparations containing ethyl cellulose are well suited for colouring nitro-cellulose varnishes and printing inks, calcium-zinc resinate printing inks, and varnishes and printing inks in which ethyl cellulose is used as a binding agent. Pigment preparations containing alcoholsoluble nitrocellulose are well suited for colouring, for instance, such compositions as alcohol soluble nitro-cellulose printing inks. Pigment preparations containing cellulose acetate butyrate are well suited for colouring acryl varnishes.

As an indication of suitable combinations of solvent and resin, when the resin is a vinyl chloride vinylacetate copolymer the organic liquid may be benzene or a mixture of xylene and methyl isobutyl ketone. When the resin is polyvinyl butyral the organic liquid may be xylene. When the resin is cellulose acetate butyrate the organic liquid may be benzene. When the resin is polyvinyl chloride the organic liquid may be dichlorobenzene. When the resin is ethyl cellulose the organic liquid may be a mixture of xylene with

benzene or a mixture of xylene with petrol 100/140°C.

The provision of pigment compositions having such high organic pigment contents as 70% increases the possibility of varying the composition of the final product such as a paint, varnish, printing ink or coloured plastic since a given final pigment content can be maintained even when a greater addition of binding agents or additives are required. When producing pigmented paints, varnishes, printing inks, plastics or plastic-wares the resin-containing pigment preparation produced according to the present invention is dispersed in ground condition or without previous grinding in the binding agent in question or in one or more of the components thereof (in which latter case the manufacture of the pigmented product must later on be completed by addition of the components failing). If the pigment preparation is used in ground form a grain interval of 20-500 μ is in many cases sufficient which can be obtained easily and cheaply. If it is applied in the form of grains or in lenticular form a dimension of 3-4 mm should generally not be exceeded.

Pigmented paints, varnishes, printing inks and plastics produced by this method permit a far better utilization of the pigments than corresponding products pigmented by means of dry pigments. Thus the colour is brighter and has no grainy structure. This difference is recognizable even if the dispersion process used in the production (thereby using a pigment preparation produced according to the invention) has been fulfilled within not more than 15 minutes by stirring with a rapidly rotating stirrer. Comparable dry pigment powders must be dispersed in the same dispersing agent by a process consisting in grinding for two days in a ball mill.

In the following the invention will be illustrated by means of a number of examples.

Example 1

Into a 5 liter ball mill are introduced 1000 g of phthalocyanine blue filtercake, 30% β - copper - phthalocyanine (C.I.Pigment Blue 15), 800 g of water and 7000 g of steel balls (1.7 cm in diameter). The ball mill is closed and agitated for half an hour after which 40 g of xylene are added and the agitation is continued for one further hour whereafter 100 g "Mowital" B 30 H (a powdery polyvinylbutyral produced by Hoechst) are added. "Mowital" is a trade mark.

The ball mill is now agitated for further 16-20 hours, after which it is washed out with water and the product is isolated by filtration and dried.

There is obtained 395 g of pigment preparation in the form of glossy shells having a diameter of about 1 mm. In the example crystallisation - stabilized

α -copper-phthalocyanine may be substituted for the same amount of β - copper - phthalocyanine if at the same time the proportion of xylene is increased from 40 to 50 grammes.

Example 2

Into a 5 liter ball mill are introduced 300 g of phthalocyanine green (C.I.Pigment Green 7), 1500 g of water, 100 g of "Mowital" B 30 T and 7000 g of steel balls (diameter: 1.7 cm) after which the ball mill is closed and agitated for 6 hours. Then 100 g of xylene are added and the ball mill is agitated for 16 hours after which it is washed out with water and the product is removed by filtration and dried. There is obtained 395 g of a dark powder consisting of 75% pigment and 25% polyvinylbutyral.

Example 3

Into a 5 liter ball mill are introduced 300 g of Lithol ruby (C.I.Pigment Red 57/Ca), 1500 g of water, 75 g of xylene and 1500 g steel balls (diameter: 1.7 cm). The ball mill is agitated for 1-2 hours after which 100 g of "Mowital" B 30 H are added. After further agitation of the ball mill for 16-20 hours the product is removed by flushing and separated by filtration and dried. There is obtained 395 g of lenticular shells having a diameter of 2-3 mm. These shells, consisting of 75% pigment and 25% polyvinylbutyral, are easily pulverised. In this example lack red C (C.I.Pigment Red 53/Ba) or a Lithol red 2BM (C.I.Pigment Red 48/Mn) may be substituted for Lithol ruby.

Example 4

Into a 5 liter ball mill are introduced 300 g of Benzidine yellow G.R. (C.I.Pigment Yellow 13), 1500 g of water, 100 g of "Pioloform" BL 18 (a trade mark for a polyvinylbutyral resin sold by Wacker Chemie) and 7000 g of steel balls (diameter: 1.7 cm). The ball mill is closed and agitated for 1-2 hours after which 60 g of xylene are added and the mill agitated for 16-20 hours. The product obtained is removed by flushing with water and separated by filtration and dried. There is obtained 395 g of lenticular shells, diameter 1/2-1 mm.

Example 5

Into a 5 liter ball mill are introduced 300 g of carbon black (C.I.Pigment Black 7), 1600 g of water, 100 g of "Mowital" B 30 H and 7000 g of steel balls (diameter: 1.7 cm). The ball mill is closed and agitated for 1-2 hours after which 100 g of xylene are added and agitated for 16-20 hours. The resulting product is washed out from the mill with water, removed by filtration and dried. There is obtained 395 g of pigment preparation in the form of glossy grains (1/2 mm) consisting

of 75% pigment and 25% "Mowital" B 30 H.

Example 6

5 Into a 5 liter ball mill are introduced 450 g of phthalocyanine blue (β -copper phthalocyanine) (C.I.Pigment Blue 15), 1450 g of water and 7000 g of steel balls (diameter: 1.7 cm). The ball mill is closed and agitated for 1 hour after which 75 g of xylene and 75 g of methyl isobutyl ketone are added. Grinding is continued for 1 hour after which 150 g of vinylit VYHH (a powdery Copolymerisate of vinylchloride and vinylacetate produced by Union Carbide and Carbon Corporation) are added. The ball mill is now agitated for 16-20 hours after which the resulting product is removed by washing with water, isolated by filtration and dried. There is obtained 594 g of a dark powder consisting of 75% of pigment and 25% of vinylit VYHH.

Example 7

25 Into a 5 liter ball mill are introduced 450 g of permanentgelb HR (C.I.Pigment Yellow 83) (a benzidine yellow produced from Hoechst), 1350 g of water, 75 g of xylene, 75 g of methyl isobutyl ketone and 7000 g of steel balls. The ball mill is closed and agitated for 1-2 hours after which 150 g of vinylit VYHH are added. Grinding is continued for 16-20 hours after which the ball mill is opened and the resulting product is removed by washing with water, filtration and drying. There is obtained 594 g of a yellow powder consisting of 75% pigment and 25% vinylit VYHH.

Example 8

40 Into a 5 liter ball mill are introduced 300 g of Lithol red 2 BM (C.I.Pigment Red 48/Mn), 1500 g of water, 100 g of vinylit VYHH and 7000 g of steel balls (diameter: 1.7 cm). The ball mill is closed and agitated for 4 hours after which 150 g of benzene are added. After further agitation for 20 hours the ball mill is opened, the product is removed by washing out with water, filtration and drying. There is obtained 396 g of granules of a diameter ranging between 1/2-1 mm and consisting of 75% pigment and 25% vinylit. The granules are easily pulverized.

Example 9

50 Into a 5 liter ball mill are introduced 300 g of benzidine yellow GG (C.I.Pigment Yellow 17), 1500 g of water, 100 g of vinylit VYHH and 7000 g of steel balls. The ball mill is agitated for 1-2 hours after which 50 g of xylene and 50 g of methyl isobutyl ketone are added. After continued agitation for 16 hours the ball mill is opened and the resulting product is washed out with water, filtered and dried. There is obtained 396 g of glossy, coarse powder, consisting of 75% pigment

and 25% vinylit. The granules are easily pulverized.

Example 10

65 Into a 5 liter ball mill are introduced 300 g of phthalocyanine green (C.I.Pigment Green 7), 1500 g of water, 100 g of vinylit VYHH and 7000 g of steel balls. The ball mill is closed and agitated for 2 hours after which 50 g of xylene and 50 g of methyl isobutyl ketone are added. The ball mill is then agitated for a further 16-20 hours after which the resulting product is washed out with water, filtered and dried. There is obtained 395 g of dark shells having a diameter ranging between 1 and 2 mm and consisting of 75% pigment and 25% vinylit.

Example 11

80 Into a 5 liter ball mill are introduced 200 g of pyrazolon orange (C.I.Pigment Orange 34), 1500 g of water, 400 g of vinylit VYHH and 7000 g of steel balls (diameter: 1.7 cm). The ball mill is closed and agitated for 2 hours. Then 70 g of xylene and 70 g of methyl isobutyl ketone are added. The agitation of the ball mill is continued for a further 16-20 hours after which the resulting product is removed by flushing with water, filtered and dried. There is obtained 594 g of lenticular shells having a diameter of 2-3 mm and consisting of 1/3 pigment and 2/3 vinylit.

Example 12

95 Into a 5 liter ball mill are introduced 300 g of Carbon Black (C.I.Pigment Black 7), 1500 g of water, 65 g of xylene, 65 g of methyl isobutyl ketone and 7000 g of steel balls. The ball mill is agitated for 1-2 hours after which 300 g of vinylit VYHH are added. After a further 1 hour's milling, 25 g of methyl isobutyl ketone are added. The agitation is continued for further 16-20 hours after which the ball mill is flushed out with water and the resulting product is removed by filtration and dried. There is obtained 594 g of granules measuring 1/2-1 mm and consisting of 50% pigment and 50% resin. The granules are easily pulverized.

Example 13

110 Into a 5 liter ball mill are introduced 375 g of benzidine yellow GR (C.I.Pigment Yellow 13), 1500 g of water, 125 g of ethyl cellulose Nlo, in the form of powder (Hercules) and 7000 g of steel balls. The ball mill is closed and agitated for 1 hour. 85 g of petrol, 100/140°C, are added and the ball mill is further agitated for half an hour after which 50 g of xylene are added. Grinding is now continued for 16-20 hours after which the resulting product is washed out with water, filtered and dried. There is obtained 495 g of crystalline powder consisting of 75% pigment and 25% ethyl cellulose.

Example 14

5 Into a 5 liter ball mill are introduced 400 g of phthalocyanine blue (β -copper phthalocyanine) (C.I. Pigment Blue 15), 1700 g of water, 100 g of xylene and 7000 g of steel balls. The ball mill is closed and agitated for 1 hour. 100 g of ethyl cellulose N10 are added. Grinding is continued for 16-20 hours after which the product produced is washed out with water, filtered and dried. 495 g of a crystalline powder consisting of 80% pigment and 20% ethyl cellulose are obtained.

Example 15

15 375 g of Lithol ruby (C.I. Pigment Red 57/Ca), 1550 g of water, 125 g of ethyl cellulose N10 and 7000 g of steel balls are introduced into a 5 liter ball mill. Agitation for 1 hour, after which 120 g of petrol 100/140 are added and grinding continued for half an hour, after which 50 g of benzene are added. The ball mill is now agitated for a further 16-20 hours, after which the resulting product is washed out with water, filtered and dried. There results 495 g of a crystalline powder consisting of 75% pigment and 25% ethyl cellulose.

Example 16

30 300 g of phthalocyanine blue (β -copper phthalocyanine) (C.I. Pigment Blue 15), 1200 g of water, 7000 g of steel balls and 60 g benzene are introduced into a 5 liter ball mill. The mill is agitated for 1 hour, after which 100 g of cellulose acetate butyrate, having a viscosity of 1/2 sec. as measured by viscosimeter according to Eastman, are added. Agitation is now continued for 16-20 hours, after which the resulting product is removed by flushing with water, filtered and dried. There is obtained 396 g of fine shells consisting of 75% pigment and 25% of cellulose acetate butyrate.

Example 17

45 Into a 5 liter ball mill are introduced 300 g of phthalocyanine blue (β -copper phthalocyanine) (C.I. Pigment Blue 15), 1500 g of water, 7000 g of steel balls and 100 g of Vestolit (a polyvinyl chloride product from Hoechst). The ball mill is agitated for 2 hours, after which 100 g of dichloro benzene are added. 50 The ball mill is agitated for 16-20 hours, after which the resulting product is flushed out from the mill with water, filtered and dried. There is obtained 396 g of a dark powder consisting of 75% pigment and 25% PVC.

Example 18

55 300 g of phthalocyanine blue (β -copper phthalocyanine) (C.I. Pigment Blue 15), 1500 g of water and 154 g of nitro-cellulose RF 10, 65% (ethanol wetted nitrocellulose from Bofors) are stirred up into a glass containing 3 liters by means of a rapidly rotating

stirrer. While still continuing the stirring the following constituents are added in the order mentioned: 70 g of xylene, 30 g dibutylphthalate and 70 g methyl isobutyl ketone. The mixture is poured into a 5 liter ball mill and 7000 g steel balls are added, after which the ball mill is agitated for 16-20 hours. The resulting product is flushed out of the mill with water, filtered and dried. There is obtained 325 g of a dark powder consisting of 70% pigment, 23% nitrocellulose and 7% dibutylphthalate.

Example 19

75 187.5 g of aqueous phthalocyanine green filtercake (C.I. Pigment Green 7), 32%, are stirred in a Greave's mixer with a solution of 6 g diamine BG (Liljeholmens Stearinfabrik AB), and 3 g glacial acetic in 50 g water. Stirring is continued for 20 minutes. Then 90 G vinylit VYHH are added and stirring is intensified for 20 minutes. While continuing the stirring 40 g xylene and 40 g methyl isobutyl ketone are added and stirring is continued for further 20 minutes. 25 ml sodium hydroxide solution, 2N, are added in the course of 5 minutes, after which stirring is continued for further 20 minutes. The product resulting is removed by filtration, washed and dried. There is obtained 152 g of a dark powder consisting of about 39% pigment and about 38.5% vinyl.

Example 20

95 55.5 kg phthalocyanine blue filter cake, 36% (β -copper phthalocyanine) (C.I. Pigment Blue 15), 100 kg water and 1 kg aerosol TR (a dispersing agent produced by Hardman & Holden) are stirred by means of a rapidly rotating agitator (Greaves). 30 kg vinylit VAGH are added and agitation continued for 20 minutes. While still continuing agitation a mixture of 0.44 kg sulphuric acid, 98%, and 2 kg water are added in the course of 5 minutes, after which agitation is continued for a further 20 minutes. While stirring is still continued a mixture of 13 kg xylene and 13 kg methyl isobutyl ketone are added in the course of 10 minutes, after which stirring is continued for further 30 minutes. The resulting powder is filtered, washed and dried. There is obtained 44 kg powder consisting of 40% pigment and 60% vinylit.

Example 21

115 975 g Permanentgelb HR-filtercake, 27.7% (C.I. Pigment Yellow 83) and 325 g water are stirred in a Greave's mixer. 90 g vinylit VYHH are added and stirring is continued for 20 minutes. While the stirring is still continued a mixture of 60 g xylene and 60 g methyl isobutyl ketone are added, and stirring continued for further 50 minutes. The resulting product is filtered, washed

and dried. There is obtained 354 g powder consisting of 75% pigment and 25% vinylit.

Example 22

120 g carbon black (C.I. Pigment Black 7) and a mixture of 90 g xylene and 90 g methyl isobutyl ketone are added by means of a spatula and the mixture is left in a dissolver container (Cowles) for 24 hours with the cover closed. 1000 g water are added. The mixture is stirred with Cowles dissolver for 5 minutes, after which 180 g vinylit VYHH powder are added in the course of 5-10 minutes, while still stirring, the stirring being continued for a further 30 minutes. The resulting product is filtered, washed and dried. There is obtained 297 g black powder consisting of 40% pigment and 60% vinylit.

Example 23

283 g aqueous benzidine yellow GG filtercake, 21.2% (C.I. Pigment Yellow 17) and a solution of 6 g fat amine OL and 3 g glacial acetic acid and 110 g water are stirred in a Greaves mixer. 120 g vinylit VYHH are added, after which agitation is continued for 20 minutes. While still stirring a mixture of 50 g water and 20 ml sodium hydroxide solution, 2M, added after which agitation is continued for 20 minutes. While still agitating, a mixture of 35 g xylene and 35 g methyl isobutyl ketone are added and stirring is continued for 20 minutes. The resulting product is filtered, washed and dried. There is obtained 180 g yellow powder consisting of about 32% pigment and about 65% vinylit.

Example 24

253 g aqueous permanent carmine FBB, extra in the form of a filter cake containing 23.7% pigment (C.I. Pigment Red 146), 250 g of water and 120 g of vinylit VYHH are stirred in a Greaves mixer and stirring continued for 20 minutes, after which a mixture of 46 g xylene and 46 g methyl isobutyl ketone are added in the course of 5-10 minutes with continued stirring, which thereafter is further continued for 30 minutes. The resulting product is filtered and dried. There is obtained 178 g red powder consisting of 33 1/3% pigment and 66 2/3% vinylit.

Example 25

338 g aqueous benzidine yellow GR, filter cake (C.I. Pigment Yellow 13), 26.6%, and a solution of 9 g fat amine OL and 4 1/2 g glacial acetic acid in 170 g water are stirred in a Greaves mixer, after which 90 g ethyl cellulose N10 are added and stirring continued for 20 minutes. While stirring is still continued 9 g ammonia, 25%, and 250 g water are added in the course of about 5 minutes, after which stirring is continued for 20 minutes. Now on further stirring 59 g

petrol 110/140 are added, followed by 41 g xylene, after which stirring is continued for 30 minutes. The product resulting is filtered, washed and dried, whereby 185 g yellow powder consisting of about 48.5% ethyl cellulose and 48.5% pigment is obtained.

Example 26

278 g aqueous phthalocyanine blue filter cake (β -copper phthalocyanine) (C.I. Pigment Blue 15), 5 g aerosole TE and 500 g water are stirred in a Greaves mixer, 100 g Mowital B 30 H are added and stirring is continued for 20 minutes. While the stirring is still continued 11 ml sulphuric acid, 2M, are added and stirring is continued for 20 minutes. Now under agitation 110 g xylene are added within 5 minutes and stirring continued for 30 minutes. The product resulting is filtered, washed and dried. There is obtained 198 g dark powder consisting of 50% pigment and 50% polyvinylbutyral.

Example 27

In a 1250 liter ball mill there are introduced 120 kg steel balls (1.7 cm in diameter), 75 kg phthalocyanine blue (C.I. Pigment Blue 15) and 100 kg water. The ball mill is closed and agitated for 1 hour. After this 275 kg water are added and agitation is continued for half an hour. 8 kg xylene is added, agitation continued for 1 hour and 25 kg "Mowital" B 30 H are added. The ball mill is now agitated for 16 hours at 20-30°C, after which the resulting product is washed out of the mill, filtered, washed cautiously and dried. After drying 98 kg lenticular plates, 1/2-1 mm in diameter and consisting of 75% pigment and 25% polyvinylbutyral are obtained.

Example 28

In a 5 liter ball mill the following components are introduced: 300 g benzidine yellow G (C.I. Pigment Yellow 12), 1500 g water, 40 g petrol 100/140°C, and 7000 g steel balls (diameter: 1.7 cm). The ball mill is closed and agitated for 2 hours, after which 100 g "Pentalyn" K (a trade mark for a maleinate resin from Hercules Company) are added. Milling is continued for 16 hours, after which the resulting product is washed out with water, filtered and dried. There is obtained 197 g of a crystalline powder consisting of 75% pigment and 25% maleinate resin.

Example 29

Production of nitro cellulose printing ink based on spirits

29 g A
29 g B
8.9 g dibutyl phthalate
16.3 g isopropyl acetate
7.5 g butyl acetate
5 g ethanol

are weighed out in a 250 ml tin suitable for using connection with a small rapidly rotating stirrer. Under agitation 13.3 g pigment preparation produced according to example 2 and containing 10 g pigment (Phthalocyanine green) is added. In the above prescription the designations A, B refer to a solution of nitro cellulose and a mixture of equal parts of Arochem and ethanol, respectively.

Intensive agitation is continued for 15 minutes, after which ethanol is added for the purpose of dilution until the viscosity is 25-30 seconds measured on the DIN-cup No. 4, has been attained, which requires about 43 g of ethanol.

For the purpose of comparison with the printing ink thus produced another printing ink having the same proportion of the same pigment is produced by using the pigment in the form of powder. This is accomplished by introducing the following constituents in a ball mill:

10 g phthalocyanine green
40 g A
20 g B
8 g dibutyl phthalate
15 g isopropyl acetate
7 g butyl acetate
300 g ceramic balls

after which the ball mill is activated and remained agitated for 48 hours. Then the milled product is diluted with ethanol in the same manner as above described to obtain the viscosity of 25-30 seconds made on DIN-cup No. 4.

When the two printing inks are printed adjacent to each other on various materials such as aluminium foil, cellophane and paper, it will be found that the former is considerably more glossy and transparent than the latter.

WHAT WE CLAIM IS:—

1. A particulate pigment preparation comprising particles of a resin and organic pigment dispersed within the resin particles, the pigment being present in the particles in an amount of 70% or more by weight based on the total weight of resin and pigment.

2. A method of producing particles of resin having organic pigment dispersed within the particles, the pigment being present in the particles in an amount of 70% or more by weight based on the total weight of resin and pigment, comprising mixing together the resin in particulate form, organic pigment in an amount of 70% or more by weight based on the total weight of resin and pigment, water and an organic liquid, or organic liquid

mixture, that is immiscible with water and is incapable of dissolving the resin but which is absorbed in the resin, and thereby forming an organic solid phase comprising the resin, pigment and organic liquid or liquids, and an aqueous phase that is substantially free of organic liquid, and separating the aqueous phase from the solid phase.

3. A method according to claim 2 comprising the additional step of removing the organic solvent from the solid phase.

4. A method according to claim 2 or claim 3 in which the organic liquid or organic liquid mixture is one which has a solubility parameter value substantially immediately above or substantially immediately below the solubility parameter interval of the resin.

5. A method according to any of claims 2 to 4 in which the resin is a vinyl chloride vinyl acetate copolymer and the solvent is benzene or a xylene-methyl isobutyl ketone mixture.

6. A method according to any of claims 2 to 4 in which the resin is polyvinyl butyral and the organic liquid is xylene.

7. A method according to any of claims 2 to 4 in which the resin is cellulose acetate butyrate and the organic liquid is benzene.

8. A method according to any of claims 2 to 4 in which the resin is polyvinyl chloride and the organic liquid is dichloro benzene.

9. A method according to any of claims 2 to 4 in which the resin is ethyl cellulose and the organic liquid is a mixture of xylene with petrol 100/140°C or xylene with benzene.

10. A method according to any of claims 2 to 9 in which the mixing is conducted by ball milling.

11. A method according to any of claims 2 to 9 in which the mixing is conducted by stirring with a rotating stirrer.

12. A method according to any of claims 2 to 11 in which the water is first added to the pigment and the organic liquid and resin are added subsequently.

13. A method according to claim 2 substantially as herein described with reference to any of the Examples.

14. A particulate pigment preparation comprising particles of a resin and pigment dispersed within the resin particles obtained by a method according to any of claims 2 to 13.

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